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Al-doped VO_2 films as smart window coatings: Reduced phase transition temperature and improved thermochromic performance

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ABSTRACT

In the pursuit of energy efficient materials, vanadium dioxide (VO_2) based smart coatings have gained much attention in recent years. In this paper, we investigate Al-doped VO_2 films as thermochromic coatings on glass substrates by DC magnetron sputtering. It is found that adding Al^{3+} ions into VO_2 films can generate groups of polygonal grains and nanowire clusters, apart from routinely reducing the valence and decreasing the grain size, through XRD, XPS, Raman shift and SEM results. For optical properties of Al doped films, a blue-shift of absorption edge in transmittance spectra has been introduced, which can significantly improve the luminous transmittance. Further, largely reducing phase transition temperature and enhancing solar modulation ability are also achieved. After carefully analyzing the relationship between the film characterizations and optical performance, we attribute the advanced theromochromic properties to the generation of nanowire clusters by the depositing conditions and the transformation effect of Al dopants. Such good thermochromic performances obtained by Al doping obviously overcome the drawbacks of undoped VO_2 films for practical application. This work provides a considerable and new method of optimizing thermochromic properties of VO_2 films as smart window coatings.

1. Introduction

Vanadium dioxide (VO_2) is one of the most promising thermochromic coating materials for energy-saving "smart window" due to its fully reversible metal-insulator transitions (MIT) [1]. At the critical temperature of 68 °C for bulk material, VO_2 crystal abruptly changes from the high-temperature rutile phase ($P4_2/mnm$, R) to the low-temperature monoclinic phase ($P2_1/c$, M1), accompanied with a change from infrared-reflective metallic state to infrared-transparent insulator state [2,3]. Meanwhile, the visible transmittance almost remains constant across the phase transition [4]. Owing to the merit that films keep stable after 10^8 cycles of phase transition while bulk crystal breaks after few cycles, VO_2 films have been extensively conducted [5].

Recent years, great efforts and several methods have been devoted to prepare VO_2 films, including Sol–Gel, sputtering deposition, chemical vapor deposition, pulse laser deposition, and ion implantation [6–10]. As a practically thermochromic coating, VO_2 films are required to well meet the three criteria, i.e. high luminous transmittance (T_{lum}), large solar transmittance modulation (ΔT_{sol}), and near room-temperature transition temperature (T_C) [11]. Several solutions have been employed to acquire practical VO_2 films, although it is always difficult to improve performance from three aspects simultaneously. Among them, only depositing anti-reflective coatings, such as adding TiO_2, ZnO and SiO_2 layer can achieve enhanced T_{lum} with little sacrifice of ΔT_{sol} [12–15]. In detail, adding SiO_2 layer, The T_{lum} of VO_2 films is increased by 14.6% with a nearly unchanged ΔT_{sol} due to the significant decrease of reflectance [14]. Besides, overlapping five-layer of TiO_2/VO_2/TiO_2/VO_2/TiO_2 films improves ΔT_{sol} to 12.1% as well as maintaining a high T_{lum} of 45% [16,17]. These studies are only focused on the optical performance regardless of T_C. On the other hand, lowering T_c can be achieved by introducing metallic dopants into the crystal lattice via various methods. Especially, high-valence ions doping (such as Nb^{5+}, Mo^{6+}, W^{6+} etc.) effectively decreases the transition temperature of VO_2 films [18,19]. As the most reported dopants, W ions exhibit the most effective reduction of the phase transition temperature with ratio of 23 °C /at% [20]. However, the sharp decrease of T_C by W doping aggravates the declination of T_{lum} and ΔT_{sol} inevitably.

We notice that researches on Al doping were rare in VO_2-based

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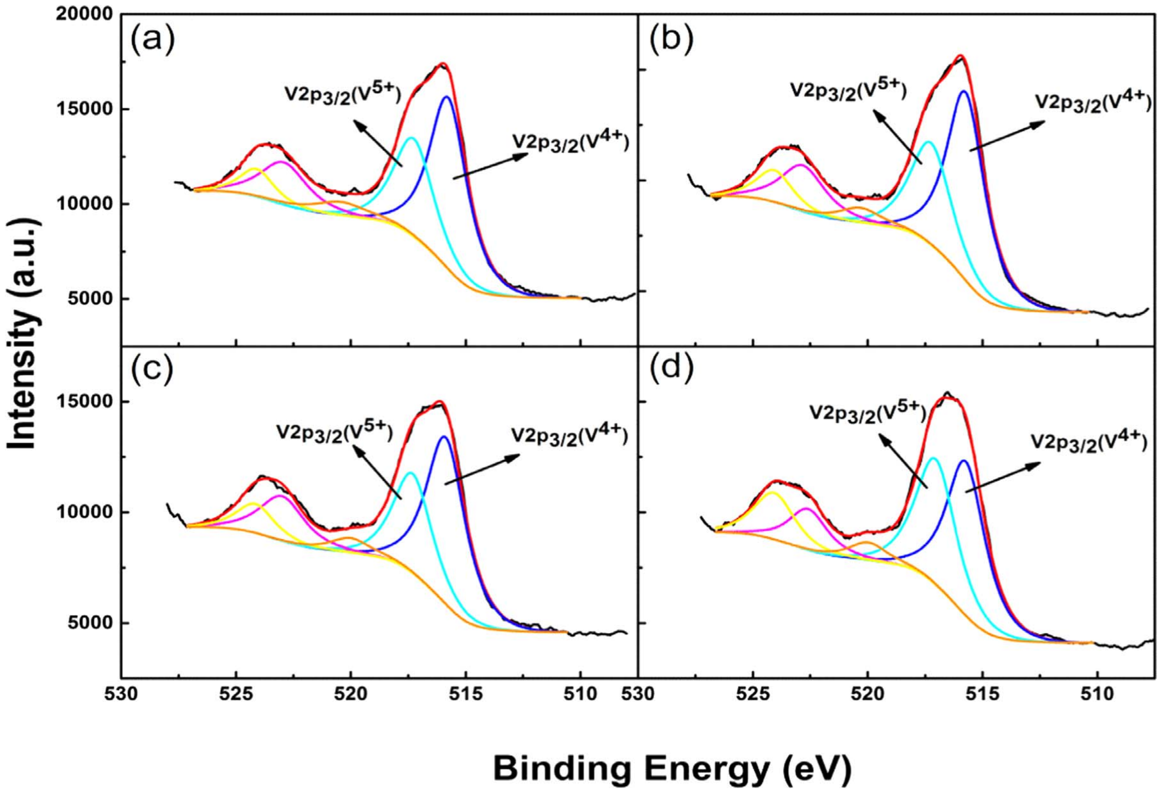

Fig. 1. XPS spectrum of VO_2 films on glass substrate with different Al/V doping ratios. (a)Al/V = 0, (b)Al/V = 0.02, (c)Al/V = 0.08 and (d)Al/V = 0.15.

smart window applications, suffering from the fact that previous reports about Al-doped VO_2 films were controversial and not investigated sufficiently. For instance, Lu et al. reported that Al-doped VO_2 films exhibited a higher transition temperature of 72 °C than pure VO_2 crystal [21]. Unfortunately, high T_C would seriously hinder the application of VO_2-based smart window. On the other hand, Chen et al. found that the transition temperature of VO_2 films were decreased to 40 °C by doping 10 at% Al^{3+} [22]. However, the study was only focused on the temperature dependence of sheet resistance. Moreover, Al doping into VO_2 films could alternate the phonon vibration modes and thus improve the modulation ability [23]. Consequently, the performance of Al-doped VO_2 films as smart window coatings needs to be systematically studied.

Therefore, we deposited Al-doped VO_2 films with different doping contents on glass substrates by DC reactive magnetron sputtering and measured its optical and MIT properties in this paper. Our results show that the best VO_2 film with the Al/V ratio of 0.08 presents a high-luminous transmittance of 47.8%, an advanced solar transmittance modulation of 7.6% which increases from 6.6% in undoped VO_2 films, and the reduced phase temperature of 44.9 °C, which is very promising for practical application.

2. Experimental details

2.1. Film preparation

The samples of both pure and Al-doped VO_2 thin films on glass substrates were prepared through DC reactive magnetron sputtering using a V: Al target. Al chips (99.99% purity, 0.8 mm thickness) were attached onto the surface of the V target (99.99% purity, 80 mm diameter, 5 mm thickness) and the Al concentration was controlled by the amount of the Al-chips. Soda-lime glass substrates were cleaned ultrasonically in diluted detergent solution, ethanol, acetone and deionized water for 15 min respectively. The substrates were finally loaded into the reactive chamber after dried by high pressure N_2 gas. The base pressure for the system was superior to 1.5×10^{-3} Pa. Meanwhile, the working gas Ar (99.99% purity) and the reactive gas O_2 (99.99% purity) were introduced separately into the chamber by using two mass flow controllers. The target was pre-sputtered in pure Ar for 15 min in order to get rid of possible contaminations of the target surface. The substrate temperature, deposition time, Ar/O_2 flow ratio and chamber pressure were kept at 78 °C, 14 min, 98/1 and 0.9 Pa, respectively. After that, ultrapure oxygen ambient was employed to a 2 h in-situ annealing treatment under a pressure of 3.3 Pa at a high temperature of 450 °C.

2.2. Film characterization

The crystal information was determined using an X-ray diffraction diffractometer (XRD, Shimadzu's XRD-7000). Raman shift spectra were performed using a 532.2 nm laser on a Raman microscope spectrometer (Horibar Corporation, LabRAM HR800). X-ray photoelectron spectroscopy (XPS, XSAM800) was applied to characterize the chemical compositions of the deposited films. The morphology of the films was determined by field emission scanning electron microscopy (FE-SEM, FEI Inspect F). The ratio of Al/V was determined by Energy dispersive spectrometer (EDS, Oxford instruments X-Max 51-XMX0019). The optical transmittance was measured at wavelengths of 280–2500 nm at temperature of 20 °C and 90 °C by a spectrophotometer (Perkin Elmer, Lambda 75) with a traditional plate heating. The hysteresis loop in transmittance was measured by UV–visible spectrometer (Shimadzu Corporation, Pharma Spec-1700) at a fixed wavelength of 1100 nm at an approximate temperature interval of 2 °C.

3. Result and discussion

Different from previous reports, Al doping in this work has been found to result in a clear reduction of phase transition temperature and a considerable enhancement of the solar modulation ability as well as an improvement of luminous transmittance. This indicates that Al-doped VO_2 films have good potential for smart window coatings